Studies on organic peroxides II : the decomposition of ethyl hydroperoxide catalysed by platinum sol (Commemoration volume dedicated to Prof. Shinkichi Horiba in celebration of his sixtieth birthday)

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STUDIES ON ORGANIC PEROXIDES. II.

The Decomposition of Ethyl Hydroperoxide catalysed by Platinum Sol.

By Sigeo Hasegawa.

It is supposed that various organic peroxides will be formed as intermediate products in the course of the oxidation of organic substances. The investigation of their properties which have not yet been known clearly seems to give us valuable informations to throw light upon the mechanisms of the oxidation and the combustion of organic substances. Recently, the decomposition and the reaction of some simple alkyl peroxide vapors have been studied to make out the mechanisms of the combustion and explosion of hydrocarbons,[1] but the reactions in liquid phase have been only qualitatively investigated by organic chemists.[2]

The present author has previously measured the velocity of the decomposition of methyl hydroperoxide, the simplest organic peroxide, in a solution catalysed by platinum sol to make clear the properties of organic peroxides.[3] It was found that methyl hydroperoxide which has a methyl radical in place of one hydrogen atom in hydrogen peroxide decomposes like the latter as expected from its constitution. On the other hand, since ethyl hydroperoxide has an ethyl radical in place of the methyl in methyl hydroperoxide, it is expected to have similar properties to hydrogen peroxide. If the equivalent reactions of these three peroxides are compared, it would be possible to know the effects of the substitution of organic radicals in hydrogen peroxide.

The present experiments were intended to make ethyl hydroperoxide decompose in a solution catalysed by platinum sol, measure its velocity by means of titration and compare the results obtained with those of hydrogen peroxide and methyl hydroperoxide.

Experimentals.

A. Materials. Ethyl hydroperoxide was prepared by a method proposed by

1) S. Medwedeff and A. Podjapolskaja, *Acta Physicochim. U. R. S. S.*, 2, 247 (1935); E. J. Harris and A. C. Egerton, *Proc. Roy. Soc., A* 168, 1 (1938); E. J. Blat, M. J. Gerber and M. B. Neumann, *Acta Physicochim. U. R. S. S.*, 10, 273 (1939); E. J. Harris, *Proc. Roy. Soc., A* 175, 273 (1939); B. V. Aivazov, N. P. Keyer and N. B. Neumann. *Acta Physicochim. U. R. S. S.*, 14, 201 (1941).

2) For example, see A. Rieche, "*Peroxyde und Ozonide*".

3) S. Hasegawa, *Rev. Phys. Chem. Japan*, 18, 33 (1944).

Rieche and Hitz.[4] 370 g of 10% hydrogen peroxide and 100 g of diethyl sulphate were well mixed, then 200 g of 40% solution of potassium hydroxide was added drop by drop during 5 hours of continuous stirring and cooling with running water. After further stirring for some hours, the solution was cooled with ice and a solution of sulphuric acid was added until it became weakly acidic. The half to two thirds of the solution was rapidly distilled on an oil bath. The ethyl hydroperoxide was extracted from the distillate with ether. The ether solution was dried with anydrous sodium sulphate. The procedure was repeated as quickly as possible to obtain a large quantity of the ether solution. The dry solution, after being filtered, was subjected to distillation at 50°C to evaporate almost all the ether contained. The raw product thus obtained was distilled on a water bath at 60°C and at lower pressure. The fraction boiling at 40 to 42°C at 55 mm pressure was used in the experiments. The density of ethyl hydroperoxide thus obtained was $d_4^{15}=0.954\sim0.956$. The peroxide was preserved as a solution of a concentration of 0.3216 mols per liter and at the experiments the stock solution was used after diluting to an adequate concentration. The experiments were performed as quickly as possible.

Platinum sol was also prepared by a method described in case of methyl hydroperoxide.[3)5)] Platinum was dispersed by high frequency alternating current and then hydrogen was passed through the sol thus obtained. The concentration of the platinum sol was $1\sim5\times10^{-4}$ g-atom per liter. The sol from the original solution was used.

B. Methods. The experimental methods were the same as those of methyl hydroperoxide. 100 cc. of an ethyl hydroperoxide solution of the proper concentration at the given temperature was decomposed with the addition of several cubic centimeters of platinum sol. At appropriate intervals the portion of 5 cc. was taken from this solution and poured into a potassium iodide solution acidified with sulphuric acid. After standing overnight, the liberated iodine was titrated with the standard sodium thiosulphate in order to estimate the undecomposed ethyl hydroperoxide. In this case, it was found also that the observed value of the peroxide by the iodometric titration was not its exact value. The deviation of the observed value from the true concentration is shown in Table I.

Only a portion of the actual quantity of ethyl hydroperoxide can be estimated, but its proportion is independent of the concentration. It is, therefore, possible to

4) A. Rieche and F. Hitz, *Ber.*, 62, 2458 (1929).
5) E. Suito, *Rev. Phys. Chem. Japan*, 13, 74 (1939); 15, 1, 155 (1941); 16, 1 (1942).

Table I.

The percentage estimated from the solution of known concentration of ethyl hydroperoxide by means of iodometry.

Concentration of C_2H_5OOH (mol/l)	Per cent observed
0.0804	68.8
0.1608	67.8
0.3216	70.1

know the relative quantity of the decrease in concentration in the course of the decomposition and so use the iodometric titration to follow the reaction.

It was confirmed that ethyl hydroperoxide was considerably stable and a spontaneous decomposition during the reaction was negligible. Further, the peroxide was not decomposed by platinum sol in the acidic potassium iodide solution. The platinum sol was also stable and the coaguration during and after the reaction was not observed.

In the experiments with hydrogen peroxide for comparing with those of ethyl hydroperoxide, it was much the same as those of ethyl hydroperoxide except that the concentration of the platinum sol used was one twentieth of the original solution and a potassium permanganate solution was used for the analysis.

Experimental Results and their Considerations.

1. Reaction Velocities and Concentrations of Ethyl Hydroperoxide.

25 cc. of platinum sol was added to 100 cc. of the ethyl hydroperoxide solutions, their concentrations being 0.0804, 0.1608, 0.2412 and 0.3216 mols per liter respectively. The results are shown in Fig. 1. In the figure, log V is plotted against t, where V is the volume of the sodium thiosulphate solution required to titrate the peroxide at the time t. The forms of log $V \sim t$ curves are similar to those of methyl hydroperoxide. The period of the curved initial stage in which log V decreases rapidly is somewhat larger, i. e. 30 to 40 minutes. The first order velocity constants of the linear main stage evaluated from the inclination of the straight part of the curve are tabulated in Table II.

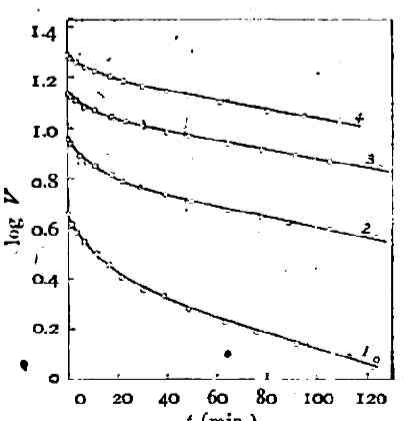

Fig. 1. The log $V \sim t$ curves at various initial concentrations of C_2H_5OOH.

The course of the reaction of ethyl hydroperoxide agrees with the expectation from the analogy of its constitution with those of hydrogen peroxide or methyl hydroperoxide. As seen from Table II, the velocity constant of the main stage is large, when the concentration is small, but the former tends to be a definite value as the latter

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Table II. The values of k of the main stage at different initial concentrations of C_2H_5OOH.

Exp. No.	Reac. temp. (°C)	Amount of Pt-sol taken. (cc.)	Initial conc. of C_2H_5OOH. (mol/l)	Duration of initial stage (min.)	k
1	40	25	0.0804	42	3.28×10^{-3}
2	"	"	0.1608	37	2.32×10^{-3}
3	"	"	0.2412	25	1.86×10^{-3}
4	"	"	0.3216	24	1.84×10^{-3}

increases. Such a tendency as this was observed in case of methyl hydroperoxide, but it was not so much remarkable. In the first report, it was supposed that when the concentration of the peroxide was low, the surface of the catalyst with considerable activity would take part in the reaction, but when the concentration of the peroxide was high, the catalyst surface would be saturated with the reactant, and therefore, somewhat weak active centers partook in the reaction and hence the reaction velocity would become small as a whole.

2. Velocities and Reaction Temperatures.

The results of experiments with 0.0804 and 0.1608 mols per liter solutions at 30, 35, 40, 45 and 50°C are given in Figs. 2 and 3. The reaction proceeds similarly as above and shows the initial and main stages. Table III shows that the inclination of the main stage from which its velocity constant is evaluated increases with the rise of temperature.

In this case, it is also seen that the velocity constant is large when the concentration of peroxide is small. Fig. 4 shows the linear relations between log k

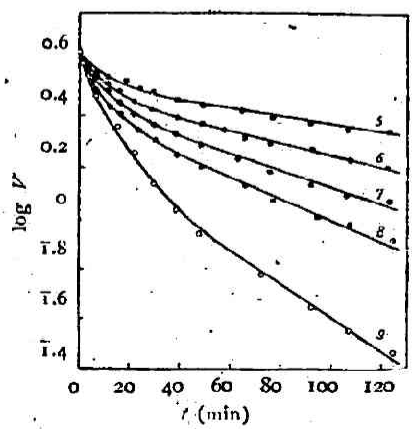

Fig. 2. The variation of log V~t curve with reaction temperature. (Initial concentration: 0.0804 mol/l).

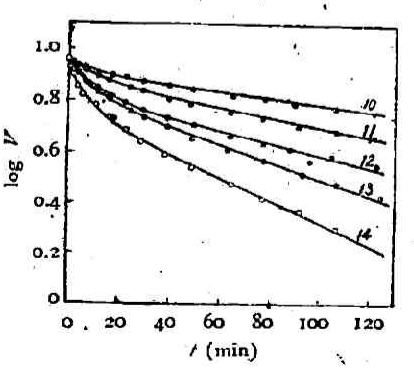

Fig. 3. The variation of log V~t curve with reaction temperature. (Initial concentration: 0.1608 mol/l).

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Table III. The velocity constants of the main stage at different temperatures.

Exp. No.	Conc. of C_2H_5OOH (mol/l)	Volume of Pt-sol taken. (cc.)	Reac. temp. (°C.)	$1/T$	Duration of initial stage (min.)	k	log k
5	0.0804	25	30	3.299×10^{-3}	38	1.48×10^{-3}	$\bar{3}.1700$
6	"	"	35	3.247×10^{-3}	39	2.35×10^{-3}	$\bar{3}.3716$
7	"	"	40	3.194×10^{-3}	42	3.28×10^{-3}	$\bar{3}.5157$
8	"	"	45	3.144×10^{-3}	42	4.30×10^{-3}	$\bar{3}.336$
9	"	"	50	3.095×10^{-3}	43	6.73×10^{-3}	$\bar{3}.8281$
10	0.1608	"	30	3.299×10^{-3}	32	1.25×10^{-3}	$\bar{3}.0969$
11	"	"	35	3.247×10^{-3}	37	1.97×10^{-3}	$\bar{3}.2936$
12	"	"	40	3.194×10^{-3}	38	2.32×10^{-3}	$\bar{3}.3646$
13	"	"	45	3.144×10^{-3}	38	3.35×10^{-3}	$\bar{3}.5256$
14	"	"	50	3.095×10^{-3}	39	4.60×10^{-3}	$\bar{3}.6623$

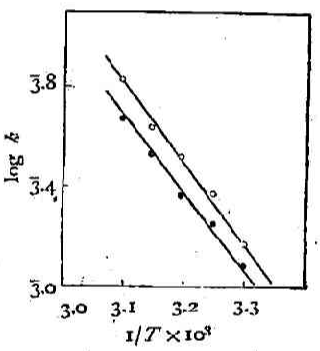

Fig. 4. The relation between log k and $1/T$.
● Initial concentration =0.0804 mol/l.
○ Initial concentration =0.1608 mol/l.

and $1/T$ for the main stage.

The apparent heat of activation calculated from this figure are 15.3 and 14.6 kcal per mol for the solutions of 0.08 and 0.16 mols per liter, respectively. It is, therefore, reasonably supposed to be 15 kcal per mol. Those for hydrogen peroxide and methyl hydroperoxide as described in the previous report are 12.0 and 14.5 kcal per mol, respectively. Since the platinum sol for the present study is not the same as those of the first report, these heats of activation cannot directly be compared with one another. Therefore, the similar reactions were performed for hydrogen peroxide using a platinum sol the concentration of which is one twentieth of the original solution. The results are shown in Table IV.

The reaction catalysed by the present sol (Sol-II) is exactly the same as that by the sol in the first report (Sol-I). The apparent heat of activation calculated from Table IV is 11.6 kcal per mol and that by Sol-I was found to be 12.0 kcal

Table IV. The velocity constant of the main stage of the decomposition of hydrogen peroxide at different temperatures.

Exp. No.	Conc. of HOOH (mol/l)	Conc. of Pt-sol. (cc/100cc sol.)	Reac. temp. (°C)	$1/T$	Duration of initial stage (min.)	k	log k
1′	0.077	0.2381	30	3.299×10^{-3}	12	8.33×10^{-3}	$\bar{4}.9207$
2′	"	"	35	3.247×10^{-3}	11	1.13×10^{-3}	$\bar{3}.0523$
3′	"	"	40	3.194×10^{-3}	9	1.51×10^{-3}	$\bar{3}.1778$
4′	"	"	45	3.144×10^{-3}	8	1.79×10^{-3}	$\bar{3}.2529$

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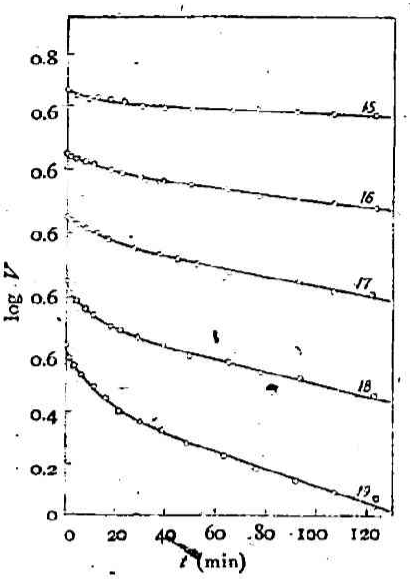

Fig. 5. The log $V \sim t$ curves at various Pt-sol concentrations.

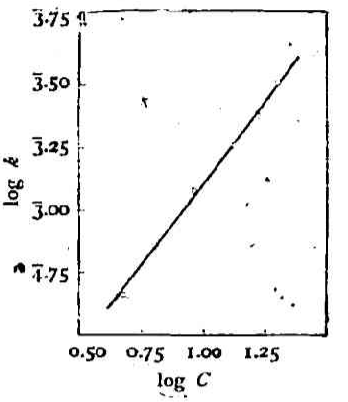

Fig. 6. The relation between log k and log C.

per mol. The agreement of these two values is satisfactory. Therefore, it may be supposed that there is no essential difference between the two sols but their concentrations.

3. Effect of the Concentrations of Platinum Sol.

The results of experiments with a 0.08 mols per liter solution at 40°C by 5, 10, 15, 20 and 25 cc. of platinum sol are given in Fig. 5 and Table V.

Table V. The effect of the variation in the Pt-sol concentration on the velocity constant of the main stage.

Exp. No.	Reac. temp. (°C.)	Initial conc. of C_2H_5OOH (mol/l)	Vol. of Pt-sol taken. (cc.)	Conc. of Pt-sol taken. C (cc/100 cc sol.)	log C	Duration of initial stage (min.)	k	log k
15	40	0.0802	5	4.76	0.6178	28	$4.52 \cdot 10^{-5}$	$\bar{4}.6551$
16	"	"	10	9.09	0.9586	38	$1.22 \cdot 10^{-3}$	$\bar{3}.0874$
17	"	"	15	13.04	1.1153	39	$1.84 \cdot 10^{-3}$	$\bar{3}.2641$
18	"	"	20	16.67	1.2217	41	$2.37 \cdot 10^{-3}$	$\bar{3}.3755$
19	"	"	25	20.00	1.3010	42	$3.28 \cdot 10^{-3}$	$\bar{3}.5157$

In this case, also, the log $V \sim t$ curve is the same as above, showing the initial and main stages. The increase in the quantity of the platinum sol not only accelerates the change in the initial stage, but also affects the velocity of the main stage in contrast to the case of methyl hydroperoxide. When log k is plotted against log C, Fig. 6 is obtained and the following relation is established.

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$$\left(\frac{k}{k'}\right)=\left(\frac{C}{C'}\right)^n \qquad (1)$$

where k and k' are the velocity constants, when the concentrations of the sol are C and C' respectively and n is a constant called the concentration exponent. The linear relation between log k and log C gives the concentration exponent n 1.308. This value is the same order of magnitude as that of hydrogen peroxide, whereas that of methyl hydroperoxide is 0.134 and much smaller than both of them.

4. Conclusions to the Decomposition of Ethyl Hydroperoxide.

It is obvious by comparison of the results of this experiment with those of the first report that ethyl hydroperoxide decomposes similarly as methyl hydroperoxide, so that the conclusions obtained for the latter should be applied to the former. 1. In the initial stage, the reaction is retarded by the reaction products. 2. The main stage of the reaction is of first order and the rate determing factor is not the diffusion volocity of reactants, but the decomposition of the peroxide on the surface of the catalyst. 3. The initial stage turns into the main one, when the activity of the catalyst becomes almost constant as a result of the retardation.

According to Rieche and Hitz,[4] the main decomposition product of ethyl hydroperoxide is ethyl alcohol and its quantity is supposed to be larger than that expected from monoxy-methyl-ethyl peroxide. From the fact that it is similar to the alkali decomposition of methyl hydroperoxide, it is considered that ethyl hydroperoxide would decompose similarly as methyl hydroperoxide, but the details are not yet made clear.

5. Comparison among Methyl and Ethyl Hydroperoxides and Hydrogen Peroxide.

In view of the above results, the three peroxides decompose similarly by platinum sol and so the reaction mechanisms would be almost the same. Let us compare the reaction velocities of these peroxides with one another.

First of all, the comparison between the activities of Sol-I and Sol-II must be made, as they were not prepared at the same time. As described above, it is supposed that the two sols differ only in their concentration and not in nature.

For hydrogen peroxide, the velocity constants k_I and k_{II} at 40°C with 5 cc. of Sol-I and Sol-II are 2.771×10^{-3} and 1.506×10^{-3}, respectively. If the equation (1) holds, in which n is equal to 1.313, then the ratio of the concentrations of the two sols is $C/C'=0.6285$ and so the calculated value assuming to use 5 cc. of Sol-I at 40°C for ethyl hydroperoxide is $k=9.209\times10^{-4}$. Table VI gives the results with 5 cc. of Sol-I at 40°C for three peroxides.

Table VI. The velocity constants of decomposition of H_2O_2, CH_3OOH and C_2H_5OOH at 40°C.

	k	n	E (kcal/mol)
Hydrogen peroxide	1.42×10^{-2}	1.313	12.0
Methyl hydroperoxide.....	8.29×10^{-4}	0.134	14.5
Ethyl hydroperoxide	9.21×10^{-4}	1.808	15.0

As seen from Table VI, the decomposition velocity of hydrogen peroxide is much greater than the others, whereas those of the latters are almost the same order of magnitude. Let us consider the reason for these differences.

The velocity of this reaction is represented by the following equation.

$$-\frac{d[P]}{dt} = k[P]$$

where k is the velocity constant of the main stage and $[P]$ the concentration of peroxide. Further, the velocity constant k is represented as follows.

$$k = Ax\varepsilon^{-E/RT}$$

where A is the area of the active surface of the catalyst, E the heat of activation, x a constant concerning the probability of reaction of active molecules. Therefore, A, E and x must be considered as to the factor affecting the reaction velocity.

In the first place, hydrogen peroxide has an activation heat much larger than the others. In this point of view, it would be easily presumed that the velocity of hydrogen peroxide is large. Methyl and ethyl hydroperoxide have almost the equal activation heats, but the latter has only a slightly larger value than the former. So far as the heat of activation is concerned, the velocity of methyl hydroperoxide must be larger than that of ethyl compound which, however, actually is rather slightly larger. Therefore, we must study the effects other than the heat of activation.

In the initial stage, the first order velocity constant decreases rapidly. This is ascribed to the retardation of the reaction which is the result of being covered over the catalyst surface by the reaction products. And it is supposed that when the surface is covered with the products, the main stage starts as a first order reaction.

As seen from the log $V \sim t$ curve (Report I, Fig. 6)[1], the periods of the initial stages for methyl hydroperoxide are about 10 to 20 minutes and their inclinations are steep, and the retardation is observed even when the concentration of the sol is small. On the other hand, since the change in the initial stage for ethyl hydroperoxide is not so steep and yet the quantity used is several times as that

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of methyl hydroperoxide, it is obvious that the retardation in the initial stage for the latter is stronger than for the former. For hydrogen peroxide, the retardation in the initial stage is scarcely observed. From these facts, it may lead to the conclusion that the retardation of methyl hydroperoxide is the strongest and becomes weak in the order of ethyl hydroxide and hydrogen peroxide.

It seems that there are some relations between the retardation and the concentration exponent of the sol, i.e. n. If the retardation is weak, the catalyst would have a considerable activity, so that the effect of the change of the sol concentration on the reaction velocity would be large, and hence n. Whereas, if the retardation is strong, the catalyst becomes less active, and so the effect of the sol concentration is less; and hence n. Therefore, the retardation for methyl hydroperoxide is presumed to be the largest. But the nature of the concentration exponent is not clear and expected not to be so simple and to change according to various factors. Actually, the exponent of methyl hydroperoxide alone is very small, whereas those of the other proxides are large in the same order. In view of their reaction progresses, however, the difference between the retardation for methyl and ethyl hydroperoxides seems to be not so large. It is obvious that the retardation for ethyl hydroperoxide is larger than for hydrogen peroxide. We can tell nothing about the nature of the concentration exponent. It seems, however, that the area A of active surface of the catalyst and hence k may be affected by the retardation. Eventually, it may be supposed that the active surface in cases of hydrogen and ethyl hydroperoxide are larger than that of methyl hydroperoxide.

x is the factor concerning the probability of decomposition of active peroxide molecules. We know nothing about it. However, it is generally supposed that the more complex the reactant molecule is, the smaller becomes x[6].

After all we observe the resultant of the above three factors as the velocity constant k. In case of hydrogen peroxide, all the factors are favourable for the decomposition and so the velocity constant is very large in comparison with the others. On the other hand, the magnitudes of the factors for methyl and ethyl hydroperoxides vary one another; hence their velocities would be of the same order.

In conclusion, it is the author's pleasant duty to acknowledge the scrupulously conscientious care with which Prefessor S. Horiba has the goodness to guide him throughout this work. Further, he has great pleasure in expressing his sincere thanks to Dr. E. Suito for his kindness to prepare the platinum sol used in this study. The cost of this research has been defrayed

6) For example, see L. P. Hammett, "*Physical Organic Chemistry*", 1940.

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